DETERMINATION OF STRUCTURAL VARIATIONS FOR A SERIES OF STEAM ACTIVATED ANTHRACITES

M. Mercedes Maroto-Valer, John M. Andrésen and Harold H. Schobert

The Energy Institute, The Pennsylvania State University,
405 Academic Activities Bldg, University Park, PA-16802, USA

Keywords: Activated carbon, anthracite, structural variations, porosity.

Although significant research has been conducted on the characterization of porosity, significantly less attention has been paid to the structural variations occurring during the activation process. Accordingly, this paper presents the structural characterization of a series of activated carbons using several analytical techniques. For this study, a Pennsylvania anthracite was steam activated in a vertical tube furnace for different periods of time. Solid yields below 60% enhanced the formation of mesopores. With increasing activation time, the atomic H/C ratios decrease and there is a significant rise in the condensation of the aromatic structures, regardless of the type of porosity developed.

INTRODUCTION

There is a continuous worldwide growing demand for the production of activated carbons, due to the increasing number of applications of these materials, especially those related to environmental protection [1]. The main reason for this expanding market is the ubiquitous use of activated carbons as adsorbent materials in a broad range of increasing applications, including both gas-phase and liquid-phase adsorption. In the US, the demand for activated carbon is forecast to increase 5-6% annually, and it is expected to reach 440 million pounds in the year 2002. The adsorptive properties of activated carbons are known to depend on both their porous and chemical structures. Although significant research has been conducted on the characterization of porosity, significantly less attention has been paid to the structural variations occurring during the activation process. Accordingly, this paper presents the structural characterization of a series of activated carbons by using several analytical techniques. For this study, anthracites were selected as precursors for the production of activated carbons. Their inherent fine pore structure makes them excellent raw materials for producing adsorbent carbons with molecular sieve properties for gas separation in pollution control technologies [2]. A Pennsylvania anthracite was steam activated in a vertical tube furnace for different periods of time. The chemical structures of the resultant series of activated samples were extensively characterized using elemental, solid state ^{13}C NMR and X-ray analyses. The structural variations determined by the above techniques were related to the adsorptive properties of the resultant activated carbons.

EXPERIMENTAL PROCEDURE

The Pennsylvania anthracite selected (Lehigh Coal & Navigation) contains ~ 6.8 % ash (db) and the atomic H/C ratio is 0.21. For this study, the anthracite was ground and sieved to generate particle size fractions of 150-250 μm and 1-3 mm. The activation set-up used consists of a vertical tube furnace, where a stainless steel tube reactor, containing around 5 g of sample, is placed. A thermocouple inserted in the reactor monitors the sample temperature. When the sample reaches the activation temperature (850°C), a flow of steam is introduced by pumping water into the reactor at low flow rates (~1.2 g/min). The porosity of

the samples was characterized conducting N_2 adsorption isotherms at 77K using a Quantachrome adsorption apparatus, Autosorb-1 Model ASIT, as previously described [3]. The elemental analyses were carried out on a Leco CHN analyzer. The solid state ^{13}C NMR measurements were conducted on a Chemagnetics M-100 instrument with a field of 2.4 T and a spinning speed of 3.5 kHz. For the quantitative single pulse excitation experiments (SPE) about 8000-14000 scans were acquired with recycle delays ranging from 60-100 seconds. As in earlier work [4], tetrakis(trimethylsilyl)silane (TKS) was used as an internal standard to determine the proportion of carbon observed by SPE. The dipolar dephasing (DD) SPE experiments were conducted using dephasing times between 1-400 μs.

RESULTS AND DISCUSSION

Development of porosity Table 1 lists the solid yields, BET surface area (SA), total pore volume (V_{TOT}) and micro- (Vmicro) and mesopore (Vmeso) volume for the activated anthracites. For the particle size fraction 150-250 μm, the solid yield decreases as the activation time increases, going from 59% to 33% after 60 and 90 minutes' activation, respectively. As expected, the larger particle size fraction presents a much higher solid yield, 79% for the 1-3 mm fraction at 90 minutes activation, compared to that of 33% for the 150-250 μm fraction. Thus, the solid yield is strongly dependent on the particle size of the precursor, with higher yields for the bigger particle size fractions. The anthracite fraction 150-250 μm activated for 90 minutes presents the highest SA and V_{TOT} (1037 m^2/g and 0.46 cc/g, respectively), while the fraction 1-3 mm activated for 90 minutes presents the lowest SA and V_{TOT} (284 m^2/g and 0.13 cc/g, respectively). These differences are strongly related to the solid yields [5]. A very good correlation has previously been obtained between the solid yields and the surface area and total pore volume, regardless of the particle size of the precursor [5].

The adsorption isotherms of the raw anthracite and the activated samples are Type I, corresponding to microporous systems. Table 1 also lists the micro- and mesopore volumes of the activated anthracites and Figure 1 shows the evolution of the micro- and mesopore volume with solid yield. For all the activated anthracites, the micropore volume is significantly larger than the mesopore volume. However, extensive gasification (solid yields < 60%) seems to promote the formation of mesopores, as illustrated by the rapid change of slope of the mesopore volume evolution (Figure 1). For instance, the mesopore volume accounts for only ~8% of the total pore volume at 59% solid yield (fraction 150-250 μm activated for 60 minutes), while the mesopore volume comprises ~19% of the total pore volume at 33% solid yield (fraction 150-1250 μm activated for 90 minutes). Previous studies have shown that the increasing formation of mesopores with decreasing solid yields are due to the removal of some pore walls and enlargement of some micropores [2].

Structural changes Table 2 lists the atomic H/C ratios for the parent anthracite and activated samples. As expected, the atomic H/C ratios decrease with activation, going from 0.21 for the parent anthracite to 0.07 for the sample activated for 90 minutes (150-1250 μm). Solid state ^{13}C NMR experiments were conducted in all the samples, using the quantitative Single Pulse Excitation (SPE) method [4]. Figure 2 shows the ^{13}C SPE spectrum for the anthracite (150-1250 μm) activated for 90 minutes. The internal standard (TKS) used for the quantitative SPE experiments gives a resonance at 3.2 ppm, while the aromatic carbon band is centered at ~122 ppm. The spectrum is dominated by the aromatic peak accounting for >99% of the total carbon. This is also the case for all the samples investigated, where the carbon aromaticity (fa) is ~1 (Table 2). The higher concentrations of paramagnetic centers expected in the activated samples did not affect the amount of carbon observed by SPE. For instance, for the anthracite (150-1250 μm) activated for 90 minutes, that is presumably the sample with the highest concentration of free radicals, over 90% of the carbon was observed by the SPE technique.

Additional structural information can be obtained by conducting NMR dipolar dephasing (DD) experiments to determine the proportions of non-protonated aromatic carbons (fnon-prot) and further calculation of bridgehead aromatic carbon [4]. Figure 3 shows the ^{13}C SPE-DD spectra for the parent anthracite, with dephasing times of 1, 40, 150 and 300 μs. The signal from protonated carbon has decayed after 40 μs, and the remaining signal is from the non-protonated aromatic carbon. The ratio of non-protonated to total aromatic carbon can be found by deconvoluting the decay of the NMR signal, as illustrated for the parent anthracite in Figure 4. The initial decay of the signal intensity is dominated by the dephasing of the protonated aromatic carbons and can be described with a Gaussian lineshape, while the longer decay is attributed to non-protonated aromatic carbon and is Lorentzian distributed. Table 2 lists the fnon-prot for all the samples investigated. With increasing activation time, there is a significant rise in the fnon-prot indicating an increase in the degree of condensation of the aromatic structures. The ^{13}C NMR structural data for all the activated anthracites will be correlated with X-ray data and the atomic H/C ratios.

CONCLUSIONS

Anthracites can easily be converted into activated carbons by steam activation. The particle size of the precursor strongly affects the solid yields of the resultant activated samples, with higher yields for bigger particle size fractions. For all the activated anthracites, the micropore volume is significantly larger than the mesopore volume. However, solid yields below 60% enhance the formation of mesopores. The SPE ^{13}C NMR experiments conducted show that with increasing activation time, there is a significant rise in the condensation of the aromatic structures, regardless of the type of porosity developed. Mechanisms that correlate the evolution of the porous structure with the chemical structure will be reported.

ACKNOWLEDGMENTS

The authors wish to thank the Consortium for Premium Carbon Products from Coal (CPCPC) at the Pennsylvania State University and the Research Council of the Basque Government for financial support. We also want to thank Lehigh Coal & Navigation Company for providing the anthracite sample.

LITERATURE CITED

1. Song, C.S. and Schobert, H.H., 1995, Fuel, **75**, 724.
2. Gergova, K., Eser, S. and Schobert, H.H., 1993, Energy & Fuels, **7**, 661.
3. Maroto-Valer, M.M., Taulbee D.N., and Schobert H.H., 1998, Prepr. Am. Chem. Soc. Fuel Division, **44**, 101.
4. Maroto-Valer, M.M., Andrésen, J.M., Rocha, D.C. and Snape, C.E., 1996, Fuel, **75**, 1721.
5. Maroto-Valer, M.M., Andrésen, J.M., and Schobert, H.H., 1999, 24th Biennial Carbon Conference, In Press.

Table 1: Yield, BET-surface areas, and total, micro- and mesopore volume for the activated anthracites [1].

	Activ. time	Yield	SA	V_{TOT}	V_{micro}	V_{meso}
	min	%	m^2/g	cc/g	cc/g	cc/g
150-250 μm	60	59	613	0.32	0.30	0.02
150-250 μm	90	33	1037	0.46	0.37	0.09
1-3 mm	60	79	284	0.13	0.12	0.01

[1] The solid yields and surface areas are expressed in ash free basis.

Table 2: Atomic H/C ratios, carbon aromaticities (fa) and proportion of non-protonated aromatic carbon (fnon-prot) for the parent and activated anthracites.

	Activ. time / min	Atomic H/C	fa	fnon-prot
Parent	--	0.21	0.99	0.76
150-250 µm	60	n.d.	1.00	0.86
150-250 µm	90	0.07	1.00	0.93

n.d.: Not determined

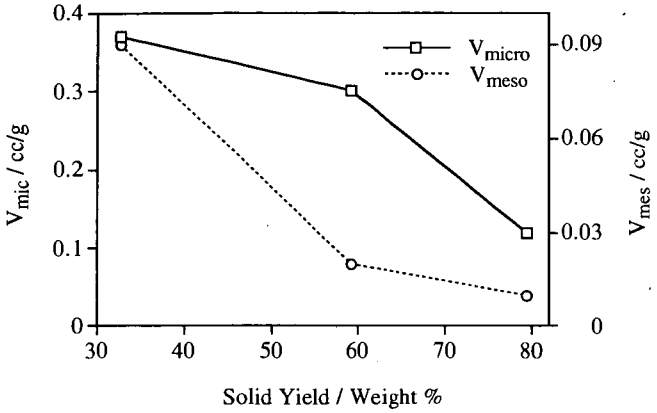

Figure 1 Evolution of the micro- and mesopore volume for the activated samples as a function of the solid yield.

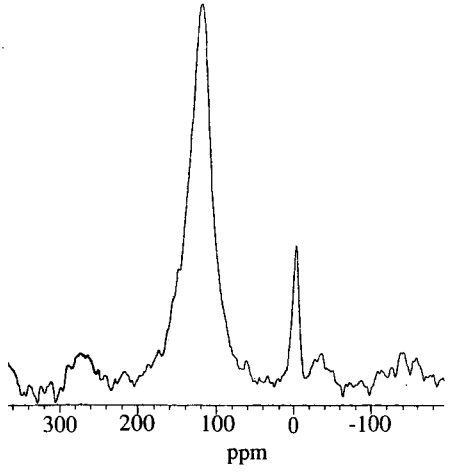

Figure 2 Solid state ^{13}C NMR spectrum for the anthracite (150-1250 µm) activated for 90 minutes using the quantitative SPE method.

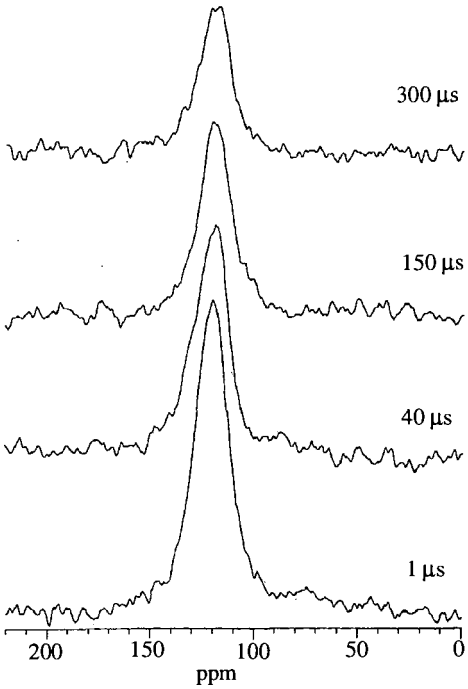

Figure 3 Spectra from SPE-DD ^{13}C NMR spectra for the parent anthracite (150-250 µm), with a dephasing time of 1, 40, 150 and 300 µs.

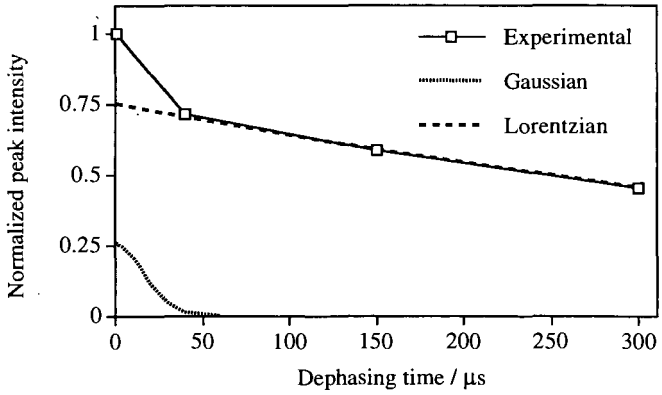

Figure 4 Plot of aromatic carbon peak intensity from the SPE dipolar dephasing experiments for the parent anthracite.